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SLIP CASTING NICKEL POWDER

by

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SUMMARY OF RESULTS

Atomized nickel powder prepared in these laboratories was slip cast in an aqueous suspension, using ammonium alginate as the dispersing agent. Slip rheology was subject to chemical control and varied with the type of acid used. Maximum densities were obtained using -325 mesh powder and sintering for 48 hour.

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INTRODUCTION

Slip casting of metal powders is an attractive method for forming metals that are difficult to work or cast by conventional methods. It is being considered as a complimentary technique to existing powder metallurgy methods and can be utilized to obtain homogeneity in alloying, to produce layer composites and complex shapes, and it is also attractive where economy, due to simple tooling, is an advantage such as in short production runs.

In order to develop some background of experience in this field, an investigation was initiated to study the slip casting of nickel powder. This powder was used because Canada is a major nickel producer and a ready supply of powder has been available since the advent of the Sherritt Gordon process.

The theory and procedure for slip casting metal powders has been discussed by several investigators[1,2,3]. Essentially the procedure is to prepare a fluid suspension of metal powder in a liquid with the aid of a dispersing agent. The resulting slip is then poured into an absorbent mould and the vehicle is absorbed by the mould, leaving a partially dried casting, which is then further dried and sintered.

MATERIALS

As a preliminary step, an apparatus was constructed for the production of atomized powder[4]. The larger particles of the powder produced were irregular in shape but they became more spherical as the size decreased. Figure 1 shows the spherical shape of the -325 mesh fraction.

Table 1 lists the densities of the different particle sizes, and Table 2 shows the combinations of particle sizes used.

TABLE 1

Density of Loose Powder

Powder Size	Bulk Density	% Theoretical Density
-100 + 150 mesh	3.4 g/cc	38
-150 + 200 mesh	3.8 g/cc	43
-200 + 270 mesh	4.1 g/cc	46
-270 + 325 mesh	4.3 g/cc	48
-270 mesh	4.8 g/cc	54
-325 mesh	4.8 g/cc	54

TABLE 2

Powder Sizes Used

Mixture	Powder Particle Sizes
A	10 wt % -100 + 150; 10 wt % -150 + 200; 10 wt % -200 + 270; 70 wt % -270
B	100% -270
C	20 wt % -100 + 150; 80 wt % -325
D	20 wt % -200 + 270; 80 wt % -325
E	20 wt % -270 + 325; 80 wt % -325
F	100% -325

The powder was prepared from electrolytic nickel and was dispersed in distilled water using ammonium alginate* as a dispersant. A 1% solution of ammonium alginate in water had a viscosity of 25 to 40 cp.

PROCEDURE

In preparing the slip, ammonium alginate was added to the metal powder and mixed in a Waring Blender for ten minutes. The resulting mixture was added to the water and stirred by hand. The percentage of ammonium alginate was calculated as a weight per cent of the water used and

*Supplied by Prescott and Company under the trade name of Protatek A150.

the amounts of water and nickel powder were calculated as a volume of water to volume of metal ratio (water/metal).

The pH of slips were adjusted by adding sodium hydroxide, acetic acid or nitric acid, and viscosities were measured with an Oswald viscometer. Prior to pouring, the slips were degassed with an aspirator and, during pouring, the mould was vibrated on a Syntron lapping and polishing machine.

The moulds were made from pottery plaster* using a ratio of 1:20 of plaster to water, and they were lined with 0.001 in. thick paper to facilitate removal of the green castings.

Slips were poured into right cylinder moulds ($\frac{1}{2}$ in. diameter by $2\frac{1}{2}$ in. long) and allowed to dry at room temperature in air for 24 hr, then at 50°C (120°F) for 3 hr. After removal from the mould, the green castings were usually sintered in hydrogen at 1100°C (2010°F) for 1 hr. They were then sealed in a quartz tube under vacuum and sintered at 1350°C (2460°F) for times up to 48 hr. The densities of the sintered castings were determined by weighing in water and in air.

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*Obtained from the United States Gypsum Company.

RESULTS

The viscosity of the ammonium alginate was first investigated. A 1% aqueous solution of ammonium alginate had a viscosity of 20 cp over a pH range of 2.5 to 11.5. When the concentration of ammonium alginate was increased to 1.8%, the viscosity was 80 cp above pH4 and increased to 400 cp below pH4; this is illustrated by the graph in Figure 2.

An attempt was also made to measure the viscosity of a mixture of nickel powder (Mixture A, Table 2) and water with a water/metal ratio of 1.3:1. At all ranges of pH the nickel powder settled out of solution and no viscosity measurements were possible.

When the same nickel powder mixture was mixed with a 1.8% aqueous solution of ammonium alginate and with the same water/metal ratio, the viscosity was 2000 cp at a pH of 7.4.

The effect on viscosity of water/metal ratios from 1:1 to 1.5:1 (Mixture A) is shown in Figure 3, and as would be expected, viscosities decreased as ratios increased.

The influence of pH on the viscosity of two slips (Mixture A) with water/metal ratios of 1.3:1 and 1.5:1 is illustrated in Figure 2. For these curves the pH was

controlled by additions of sodium hydroxide and acetic acid. Both curves show an increase in viscosity at each end of the pH range. The graph for mixture F in Figure 2 also shows that the range of pH giving constant viscosity was smaller for the finer particle size, but the general shape of the curve remained the same.

When nitric acid instead of acetic acid was used to control the pH, there was a definite change in the shape of the curves. A maximum viscosity occurred at a pH of about 6.5 and the nickel powder settled out of solution at about pH 5.8 as shown in Figure 4.

Slips for sintering were first made with mixture A. A water/metal ratio of 1.3:1, a 1.8 solution of ammonium alginate, and a pH of 7.8 to 9.8 were used and these variables were kept constant for most of the slips. In the first attempts at sintering, green castings were sintered for 2 hr at 1100°C (2010°F) in hydrogen, followed by 2 hr in argon at 1350°C (2460°F), and densities of 6 g/cc were obtained. Sintering for 4 hr in a 0.1 micron vacuum at 1350°C (2460°F) also gave densities of 6 g/cc. Then, by using all -270 mesh powder (Mixture B) and sintering in a vacuum for 4 hr a density of 6.3 g/cc was obtained.

Longer sintering times gave higher densities and sintering of mixture B for 1 hr in hydrogen at 1100°C (2010°F), then 48 hr sealed in vacuum in a quartz tube gave a density

of 7.2 g/cc. Photomicrographs in Figures 5 and 6 show the microstructure of the castings made from mixture B after sintering for 4 and 48 hr respectively. Some decrease in porosity is evident.

By decreasing the powder particle size to 20 wt % - 100 + 150 mesh and 80 wt % - 325 mesh (Mixture C), a density of 6.9 g/cc was obtained after sintering for 1 hr in hydrogen at 1100°C (2010°F) followed by 4 hr at 1350°C (2460°F) sealed under vacuum in a quartz tube. Further sintering of mixture C for times up to 48 hr gave densities up to 7.9 g/cc, as shown by the graph in Figure 7.

Photomicrographs in Figures 8 to 10 show the decrease in voids as sintering times were increased.

The densities obtained on sintering mixtures B, C, D, E and F and plotted on the 48 hr line of the graph in Figure 7 show an increase in density with decreasing powder particle size. Densities of 8.2 g/cc or 92% of the theoretical density of nickel were obtained for mixture E and mixture F. Figure 11 shows the microstructure of a casting made from mixture F sintered for 48 hr.

DISCUSSION

In the ceramics industry, where slip casting has been successfully applied, the slip consists of fine particles kept in suspension by interaction of electrical

charges acquired by adsorption of ions on the surface of particles. Rheology of the suspension is controlled by adjusting the pH which affects the ion atmosphere surrounding the particles.

One theory to explain the chemical control of rheology of slips is discussed by P.D.S. St. Pierre[5], and by A.B. Searle and R.W. Grimshaw[6]. It is based on the idea of a diffuse layer of counter ions surrounding charged particles in a slip. The interfaces of this layer of counter ions are treated as two plates of a condenser. If the potential across those plates is high the particles will repel each other and a stable suspension will be obtained. A low potential will allow coagulation due to attraction of the particles of Van der Waals' forces.

The influence of the interaction of these charged surfaces will be effective in controlling the rheology of the slip only when the forces involved are great enough to overcome the forces of gravity. Therefore, the rheology of slips containing coarse particles will be controlled by such methods as the addition of gelling agents and by varying the water/metal ratio.

Potential differences across the diffuse layer are dependent on the charge on the particles, the dielectric constant of the medium, and the thickness of the diffuse

layer which, in turn, will be dependent on such factors as the size of the counter ions.

The relationship between these variables is expressed as follows:

$$Z = \frac{4 \pi e d}{D}$$

Z - (zeta) potential difference across the diffuse layer of counter ions

e - charge on particles

d - thickness of diffuse layer

D - dielectric constant of the medium.

It should be noted that excessive additions of counter ions to a slip will cause crowding in the diffuse layer, thus reducing the effective thickness and lowering the potential.

The principles of slip casting have been applied to metal powders by P.D.S. St. Pierre[7], H.H. Hausner[8] and others. Success of this application has been attributed to the fact that most metals have an oxide coating to support electrical charges that would probably not be present on pure metal surface.

In this investigation, nickel powder of mixture A settled out of suspension in water for all ranges of pH.

This would suggest that either the particles did not support an electrical charge on their surfaces or that the particles were too large for interaction of the charges to offset the forces of gravity.

When a slip was made using mixture A and a 1.8% aqueous solution of ammonium alginate the viscosity increased to 2000 cp, the nickel powder remained in suspension and the rheology of the slip was subject to control by changes in pH.

Suspensions of spherical powders in a fluid will exhibit a higher viscosity than the suspending medium according to the equation:

$$\frac{n}{No} = 1 + \frac{1.25\ V}{1-V/0.74}^{2}$$

n = viscosity of suspension

No = viscosity of suspending medium

V = volume fraction of solid spheres

According to this equation the viscosity of the slip, when the nickel powder is added would only be about 400 cp, so a viscosity of 2000 cp could not be attributed only to mixing of the powder with the ammonium alginate solution. Also, because the viscosity of an 1.8% ammonium alginate solution is only 80 cp the increase in viscosity in the slip cannot be attributed to any gelling action.

It appears then that this increase in viscosity must be due to the ability of the ammonium alginate to form electrical charges on the powder particles or more likely to increase already existing charges.

This conclusion is strengthened by the fact that the viscosity of the slip was influenced by changes in pH, and the curves in Figure 2 (pH vs. viscosity) are typical of curves found by P.D.S. St. Pierre[7] for molybdenum, by H.H. Hausner et al[3] for stainless steel, and they are also typical of those listed by W.D. Jones[1] for thoria and uranium oxide.

When powder particles were reduced to 100% -325 mesh (Mixture F), the influence of surface charges on rheology increased, as can be seen by comparing the graph for mixture A to that for mixture F in Figure 2. Greater influence would be expected as particle sizes were further decreased.

An interesting change in the behaviour of the slips occurred when nitric acid instead of acetic acid was used to control pH. In Figure 4, the graph (pH versus viscosity) shows that a maximum as well as a minimum viscosity occurred when nitric acid was used.

Because it is improbable that the nitric acid reacted with the ammonium alginate which is stable above

a pH of 4, the severe change in viscosity when the slip became acid suggests a reaction occurred between the nitric acid and the oxide coating on the powder particles. At a pH of 5.8 it is possible that the thin layer of oxide was dissolved, exposing nickel metal that presumably would not support any electrical charge, and the nickel powder settled out of suspension.

Water/metal ratios also influenced the viscosities. With higher ratios there was less chemical control, as illustrated by the curves for ratios of 1.5:1 and 1.3:1 in Figure 2. A ratio of 1.3:1 was chosen for the slips examined because it produced a minimum viscosity of 2000 cp, having a satisfactory consistency for pouring.

Because there was no furnace available for hydrogen sintering at high temperatures, the green castings were pre-sintered at 1100°C (2010°F) in hydrogen to reduce the oxide. The castings were then sealed under vacuum in a quartz tube to protect them for further sintering at 1350°C (2460°F).

Attempts were made to obtain high densities by sintering for only 4 hr but longer times were found to be necessary, as shown by the graph in Figure 7 and the photomicrographs in Figures 5, 6, 8, 9, 10. Considerable improvement in density was obtained by decreasing the

particle size but it appears that nickel powder requires longer sintering times, as compared with the stainless steel powder for which Hausner(8) obtained up to 96% theoretical density after only 4 hr of sintering.

Some improvement in sintered densities would probably be achieved by using higher sintering temperatures, by varying the type and amount of dispersing agent and by varying the water/metal ratio.

Spherical powder was used for these experiments because it had the advantage of higher apparent density as compared to irregular-shaped powder, and H. Hausner(7) also found that spherical powder required lower water/metal ratios. Both of these properties would cause less shrinkages during fabrication.

CONCLUSIONS

1. Nickel powder can be successfully slip cast in an aqueous slip using ammonium alginate as the dispersing agent.

2. The ability to slip cast nickel powder of particle sizes used in this investigation was dependent on the use of a dispersing agent.

3. Rheology of the slips was subject to both chemical and physical control.

4. Viscosity of the slips was sensitive to the type of acid used for pH control.

5. A -325 mesh powder and sintering times of 48 hr were necessary to obtain densities 92% of metallic nickel.

ACKNOWLEDGEMENTS

This work was performed under the general direction of Mr. N.S. Spence, Head, the Nuclear Metallurgy Section.

Preparation of metallographic specimens was done by W. Hutching and W. Koops.

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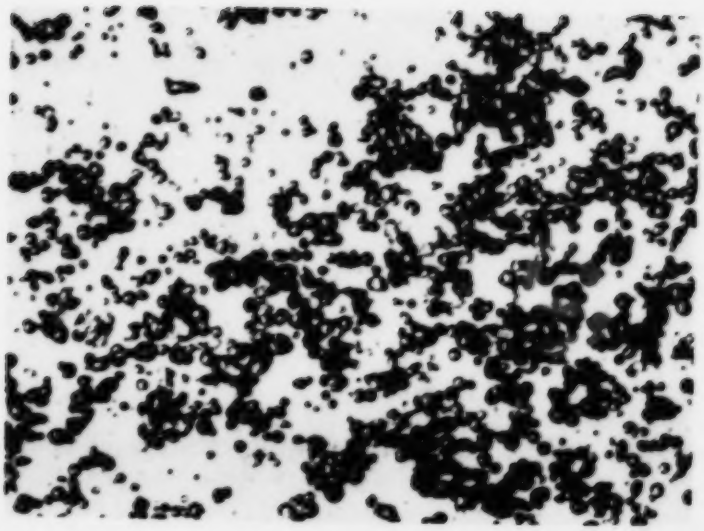

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Figure 1. Atomized Nickel Powder, -325 Mesh.

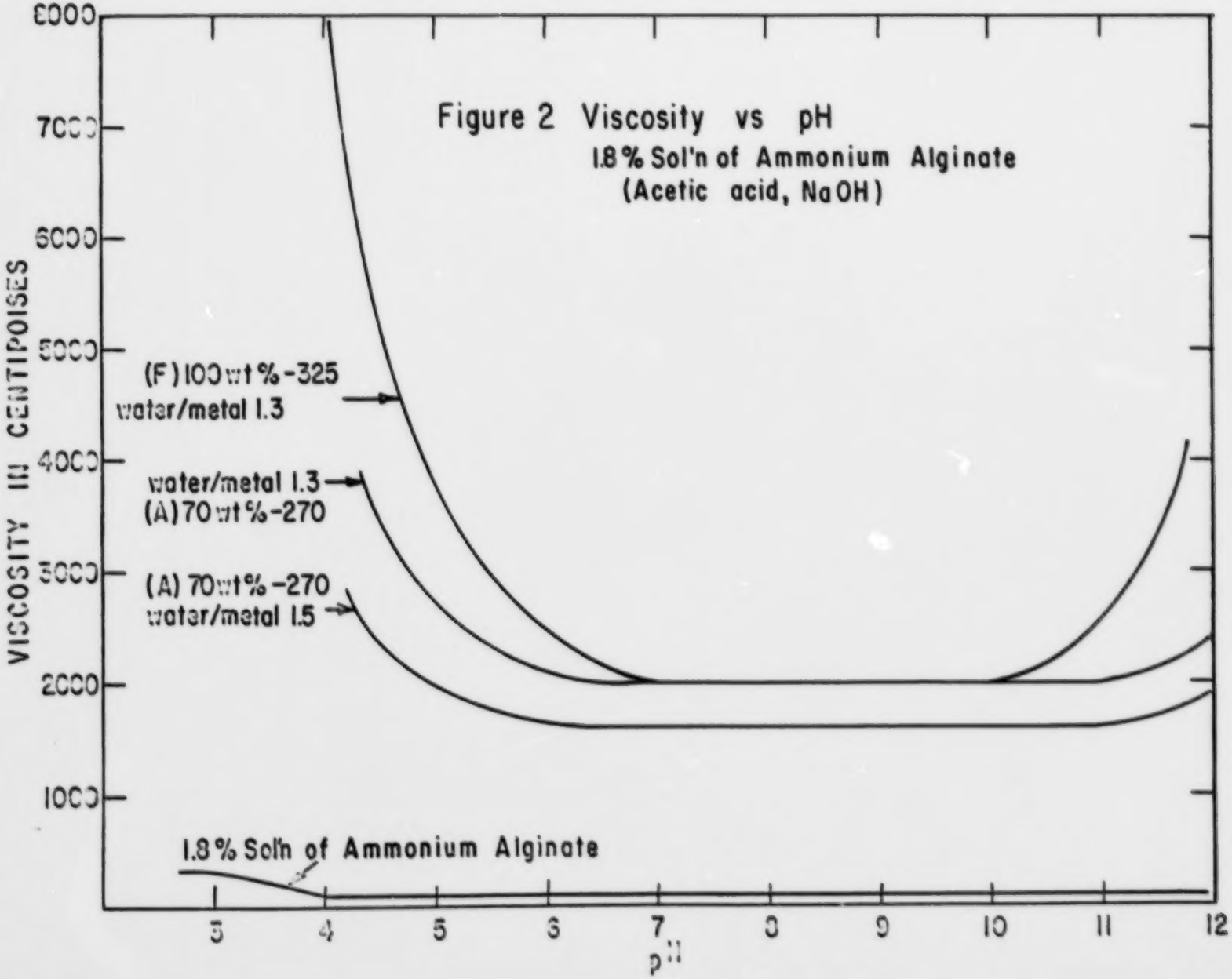
Figure 2 Viscosity vs pH
1.8% Sol'n of Ammonium Alginate
(Acetic acid, NaOH)
VISCOSITY IN CENTIPOISES
8000
7000
6000
5000
4000
3000
2000
1000
(F) 100 wt % -325
water/metal 1.3
water/metal 1.3
(A) 70 wt % -270
(A) 70 wt % -270
water/metal 1.5
1.8% Soln of Ammonium Alginate
3
4
5
6
7
8
9
10
11
12
pH

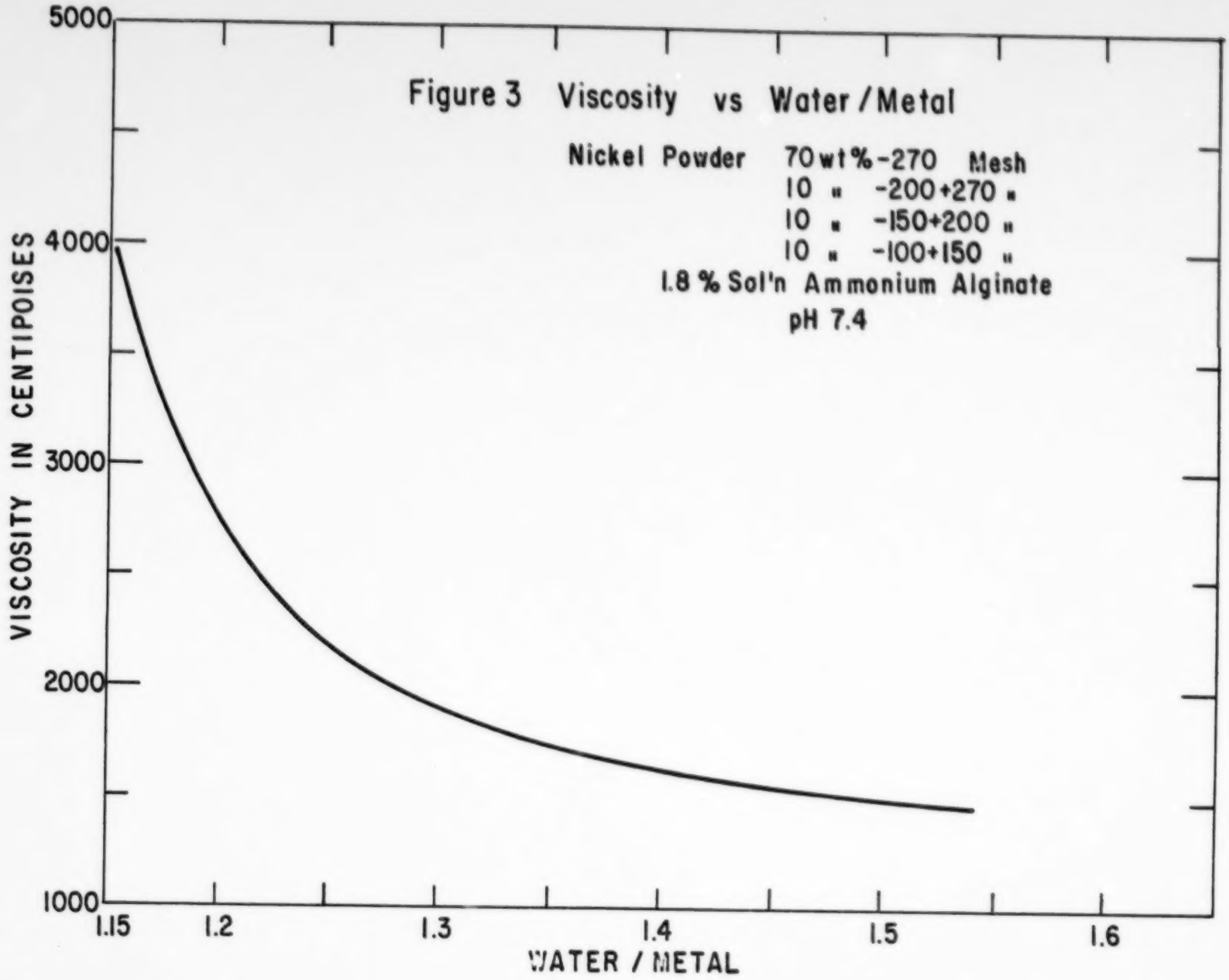
Figure 3 Viscosity vs Water / Metal
Nickel Powder 70 wt % -270 Mesh
10 " -200+270 "
10 " -150+200 "
10 " -100+150 "
1.8 % Sol'n Ammonium Alginate
pH 7.4
VISCOSITY IN CENTIPOISES
5000
4000
3000
2000
1000
1.15
1.2
1.3
1.4
1.5
1.6
WATER / METAL

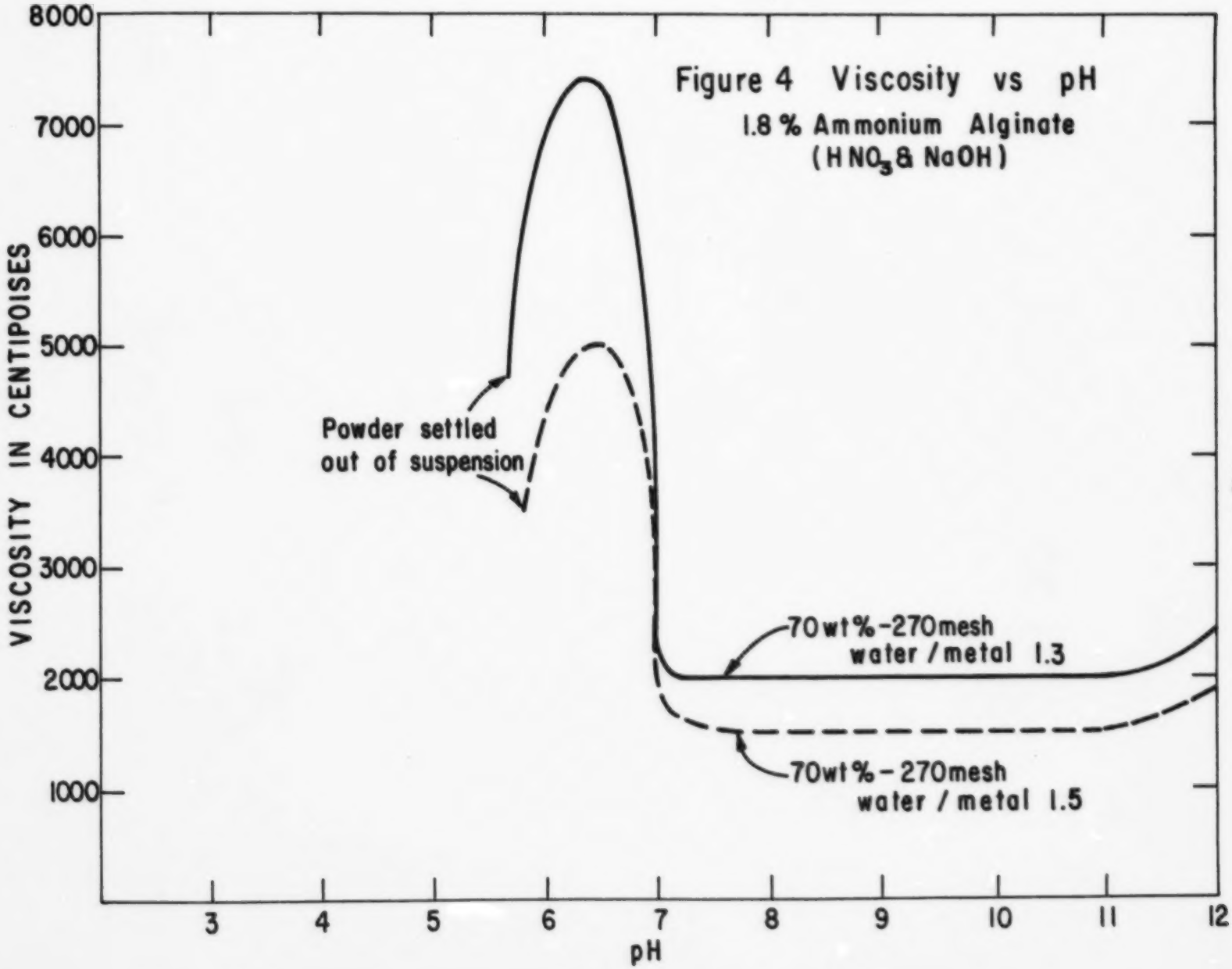
Figure 4 Viscosity vs pH
1.8 % Ammonium Alginate
(HNO3 & NaOH)
VISCOSITY IN CENTIPOISES
8000
7000
6000
5000
4000
3000
2000
1000
3
4
5
6
7
8
9
10
11
12
pH
Powder settled
out of suspension
70 wt % - 270 mesh
water / metal 1.3
70 wt % - 270 mesh
water / metal 1.5

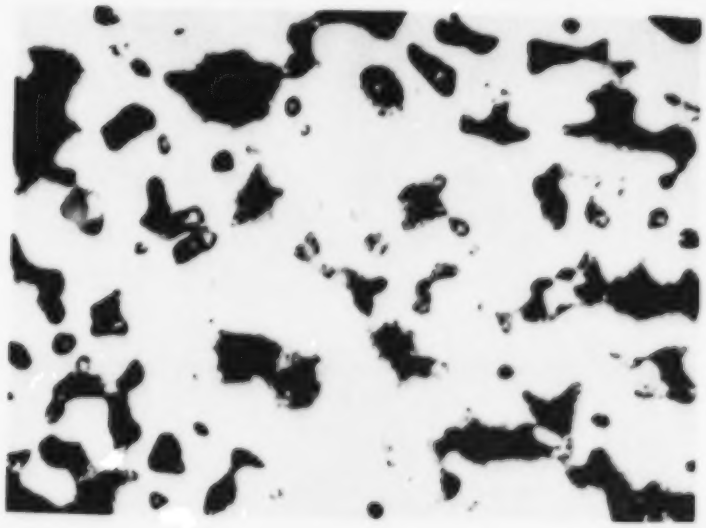

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Figure 5. Mixture B. Sintered 4 hr at 1350°C (2460°F). Etchant: Carapella's Reagent.

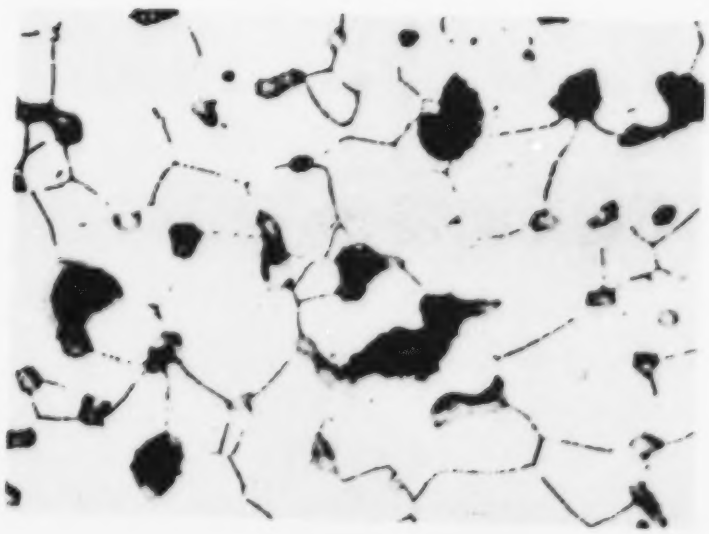

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Figure 6. Mixture B. Sintered 48 hr at 1350°C (2460°F). Etchant: Carapella's Reagent.

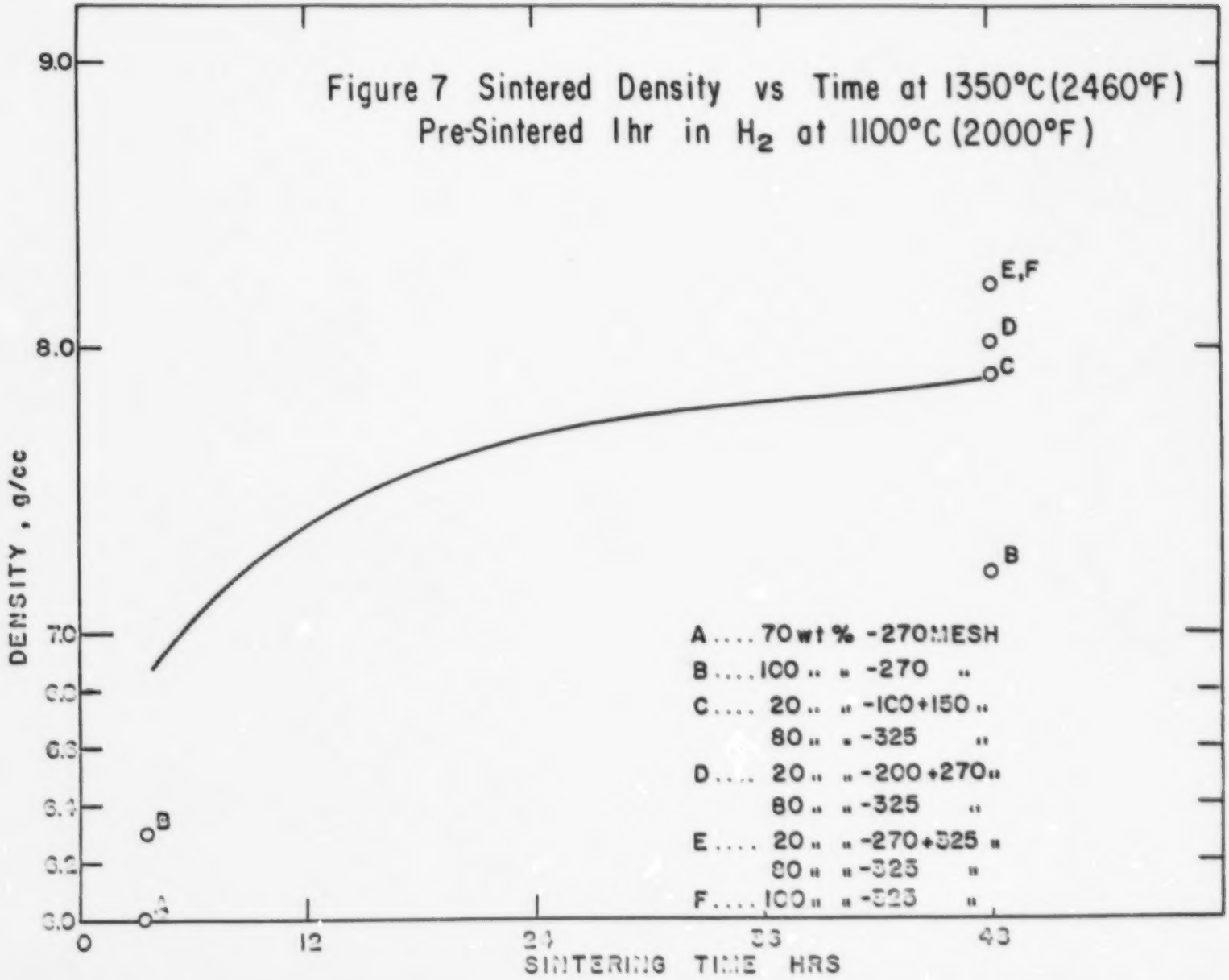
Figure 7 Sintered Density vs Time at 1350°C(2460°F)
Pre-Sintered 1hr in H_2 at 1100°C (2000°F)
DENSITY , g/cc
9.0
8.0
7.0
6.0
6.3
6.2
6.0
0
12
24
36
48
SINTERING TIME HRS
E,F
D
C
B
B
A
A....70 wt % -270 MESH
B....100 " " -270 "
C.... 20 " " -100+150 "
80 " " -325 "
D.... 20 " " -200+270 "
80 " " -325 "
E.... 20 " " -270+325 "
80 " " -325 "
F....100 " " -325 "

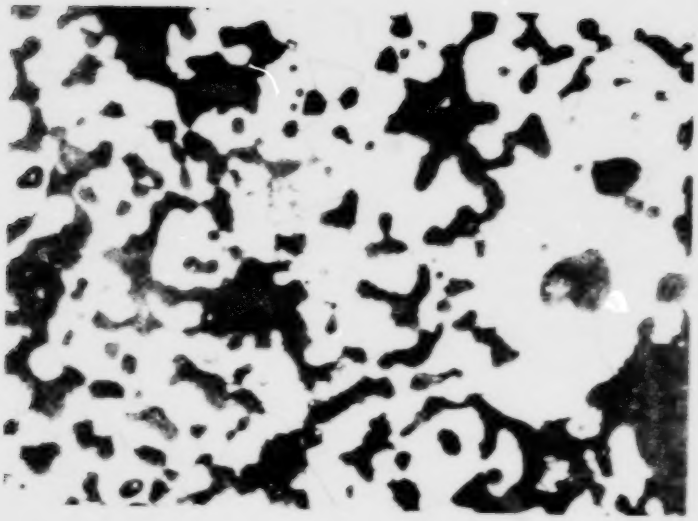

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Figure 8. Mixture C. Sintered 4 hr at 1350°C (2460°F). Etchant: Carapella's Reagent.

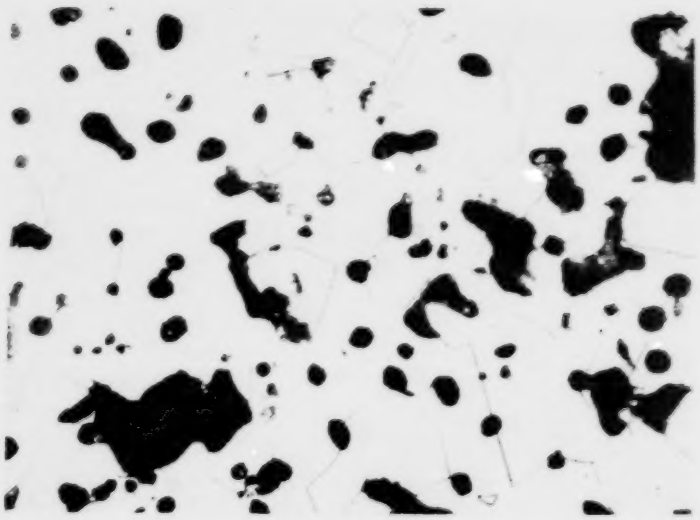

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Figure 9. Mixture C. Sintered 24 hr at 1350°C (2460°F). Etchant: Carapella's Reagent.

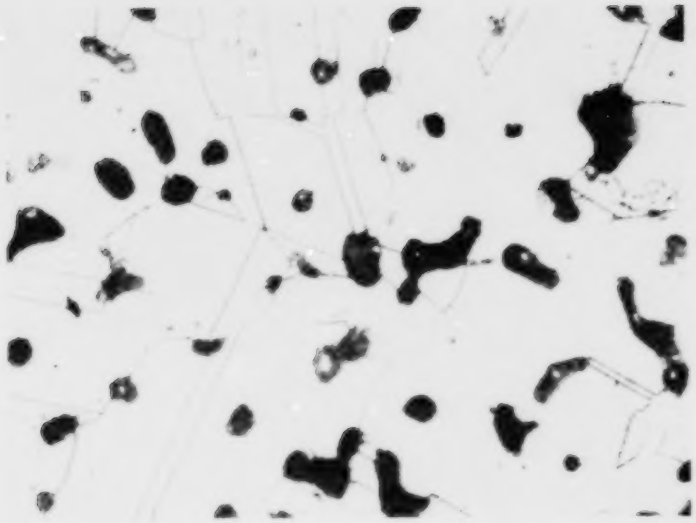

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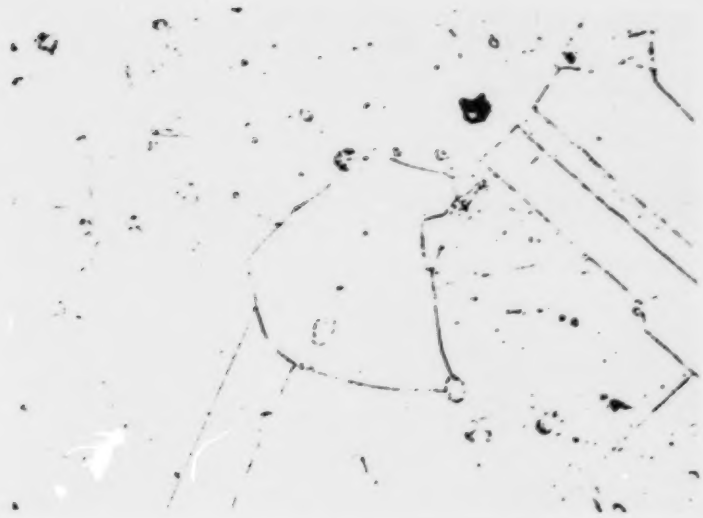
Figure 10. Mixture C. Sintered 48 hr at 1350°C (2460°F). Etchant: Carapella's Reagent.



(X250)

Figure 11. Mixture F. Sintered 48 hr at 1350°C (2460°F). Etchant: Carapella's Reagent.